Application Note 10350

Analysis of Organochlorine Pesticide Residues in Water using Gas Chromatography

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Keywords: Environmental analysis, EPA Method 508, pesticides, ECD, GC.

Introduction

Pesticides are one of the major environmental pollutants and food trace contaminants. Indiscriminate use of chemical fertilizers and pesticides has a serious impact on the environment. In particular, pesticides are increasingly used in agricultural production. The residues enter soil and water and are distributed by air due to wind and rainfall. Pesticides can pollute rivers, ground water, water in reservoirs, and are finally detected in drinking water. Also, industrial effluents carrying toxic pollutants are reported to be frequently dumped into rivers. Water drawn from reservoirs or river banks for drinking water production can become contaminated with dangerous and sometimes even up to fatal levels of contamination for human, animal, and plant life. Some compound types, especially the chlorinated pesticides like DDT, are highly persistent in the environment. Organochlorine pesticides (OCPs) are reported to be carcinogenic and mutagenic. They accumulate in the adipose tissues of animals [1]. The continuous monitoring of pollutants in water is increasingly important for food safety to avoid serious health impact. Stringent analytical controls are adopted by enforcement agencies all over the world.

For drinking water, the European Economic Community's (EEC) directive 80/778 sets the maximum admissible concentration at 0.1 µg/L for individual pesticides and 0.5 µg/L for the sum of the total detected pesticide residues [2, 3]. Hence, monitoring these pesticide residues in water at trace levels is extremely important. Capillary gas chromatography (GC) is the method of choice for monitoring OCPs in water as it is a powerful separation technique capable of resolving constituents of complex mixtures and detecting them with very high sensitivity at trace levels. Extraction, clean-up and pre-concentration techniques are used prior to chromatographic analysis of the residues of pesticides. GC with electron capture detection (ECD) is used for the analysis of residues of

halogenated pesticides and other contaminants like the polychlorinated biphenyls (PCBs).

This application describes the analytical method for analysis of OCP pesticide residues using the Thermo Scientific™ TRACE™ 1110 GC equipped with ECD and the Thermo Scientific™ AS1310 autosampler.

Experimental

Methods

Sample preparation

Several extraction methods have been reported in the literature. Liquid/liquid extraction methods are common using various solvents such as methanol, hexane, acetone, dichloromethane, and ethyl hexane, among others. The US EPA method 508 for detecting pesticide residues in water samples describes the use of dichloromethane (DCM) for extraction [4]. After liquid/liquid extraction from water, the DCM phase is separated, evaporated, and the residue re-dissolved in methyl-tert-butylether (MTBE), and injected into the GC.

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In this method, a pesticide standard with the concentration of 100 ppb has been prepared by dilution from a commercial EPA 508 pesticides residues mix. The set of OCP compounds was chosen for the special importance for drinking water analysis in India. One liter of water was spiked with 1 mL of this 100 ppb pesticide residues standard and extracted as described in the EPA method 508. The extract was finally concentrated to 1 mL, transferred to autosampler vials and analyzed.

TRACE 1110 GC Analytical Conditions

In this simple method setup, the analytes of interest can be detected at the required sensitivity level of 0.1 ppb in water using the split mode due to the excellent sensitivity of the TRACE 1110 GC ECD detector. This setup as shown in Table 1 provides distinct analytical and economic advantages. The method setup in split mode allows a higher oven start temperature, which results in a shorter analysis time for increased sample throughput. In addition, the best possible separation amongst some closely eluting peaks can be achieved by preserving conditions for high sample throughput.

Table 1. Analytical conditions

Injector module	Split/ splitless injector
Injector temperature	270 °C
Injection mode	Split
Sample volume	1 µL
Split flow	30 mL/min
Analytical column	Thermo Scientific™ TRACE™ TR-5 MS, 30 m x 0.25 mm x 0.25 µm (P/N 260F142P)
Carrier gas	Helium (99.999% purity)
Flow rate	3 mL/ min
Oven program	200 °C, 6 min
	3 °C/min to 240 °C, 10 min hold
ECD detector temperature	300 °C
Make up gas	Nitrogen (99.999% purity)

Results and Discussion

Using the TRACE 1110 GC, the acquired chromatogram of the organochlorine GC of the organochlorine pesticide residues extracted from a spiked drinking water sample is shown in Figure 1. The concentration level of the analyzed OCPs in water was 0.1 ppb or less for each of the pesticide components, as seen in Table 1. These results demonstrate the excellent sensitivity and capability of TRACE 1110 GC.

Table 2. Pesticide residue concentration as extracted from a spiked water sample.

RT [min]	Component Name	Concentration [ppb]
3.677	Alpha BHC	0.087
4.343	Beta BHC	0.095
4.465	Gamma BHC	0.096
5.455	Delta BHC	0.095
6.667	Heptachlor	0.101
8.157	Aldrin	0.094
10.068	Heptachlorepoxide	0.096
11.912	Endosulphan A	0.101
13.232	4,4'-DDE	0.156
13.363	Dieldrin	0.169
14.540	Endrin	0.110
15.352	4,4'-DDD	0.093
15.705	Endosulphan B	0.080
16.190	4,4'-DDT	0.081
17.512	Endrinaldehyde	0.098
17.733	Endosulphansulphate	0.095

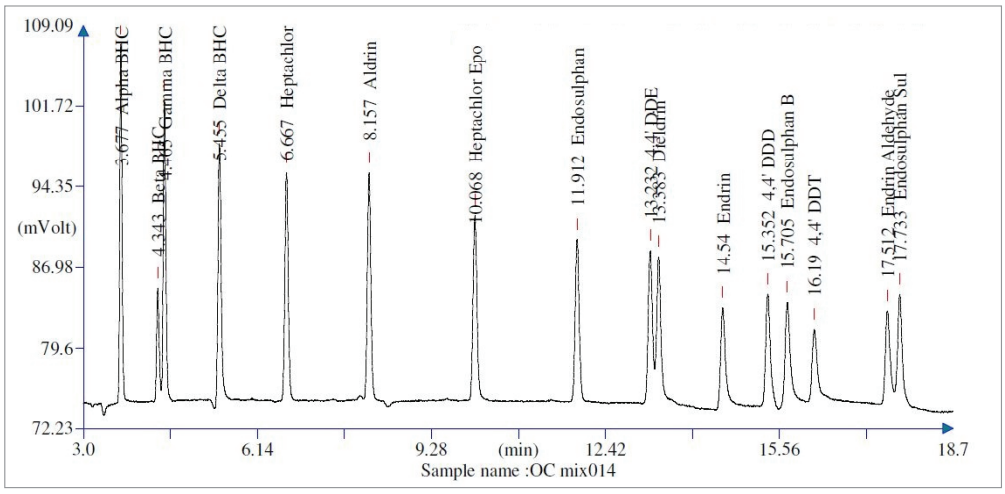

Figure 1. Chromatogram of organochlorine pesticide residues extracted from spiked water.

Linearity and repeatability

As a representative OCP compound, the linearity of lindane (benzene hexachloride, BHC, alsohexachlorocyclohexane, HCH) was studied. The results are given in Table 3.

Table 3.Linearity and repeatability results for lindane.

Concentration [ppb]	Peak Area [cts]	Avg. Area [cts]	SD [cts]	RSD [%]
10	173134			
10	170202	171252	1633	0.95%
10	170420			
25	450318			
25	438245			
25	462614	450773	8876	1.97%
25	454272			
25	448418			
50	690072			
50	729388	712403	19059	2.68%
50	703068			
50	727084			
75	1012635			
75	1020190	1030892	18074	1.75%
75	1052885			
75	1037858			
100	1332265			
100	1371105	1350959	32711	2.42%
100	1315206			
100	1385260			

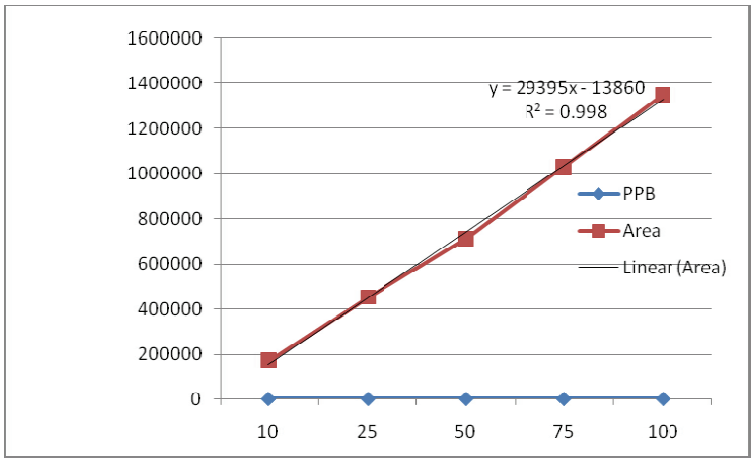

Figure 2. Linearity and precision of the lindane calibration with R^2 0.998

Repeatability for a pesticide residues mix

Repeatability of the area counts for some of the pesticide residues extracted from water samples at 0.1 ppb are given in tables 4 and 5.

Table 4. Repeatability of area counts for some pesticide residues

Pesticide	Alpha BHC [area cts]	Beta BHC [area cts]	Gamma BHC [area cts]	Delta BHC [area cts]	Heptachlor [area cts]	Aldrin [area cts]
	869761	292735	813270	884149	758437	845006
	894464	348665	892967	855364	764750	811209
	890407	300878	828299	888894	785052	855954
	877441	302595	841061	932563	811621	827178
	893057	306931	846985	893469	795061	849871
	888160	303532	838567	913912	781036	836357
Avg.	885548	309222	843524	894725	782660	837596
SD	8956	18160	24611	24140	17834	14994
%RSD	1.0 %	5.9 %	2.9 %	2.7 %	2.3 %	1.8 %

Table 5. Precision of area counts for some pesticide residues

Pesticide	Heptachlor Epoxyd [area cts]	Endosulphan A [area cts]	4,4' DDE [area cts]	Dieldrin [area cts]	Endrin [area cts]	4,4' DDD [area cts]
	740462	681686	627595	647252	502172	514653
	765479	685349	647548	675709	501904	508068
	760854	691428	664885	678555	514475	544636
	740575	678959	671731	680656	503610	555028
	766424	702275	675226	676146	517803	543167
	741306	678960	660332	661068	499133	539508
Avg.	752517	686443	657886	669898	506516	534177
SD	11864	8280	16185	11932	6998	16913
%RSD	1.6 %	1.2 %	2.5 %	1.8 %	1.4 %	3.2 %

Conclusion

The TRACE 1110 GC equipped with an ECD detector, a TRACE TR-5 MS capillary column, and the AI/AS 1310 autosampler, as chosen per the guidelines given in the US EPA method 508 is a highly sensitive and reliable solution for the analysis of common halogenated OCP pesticide residues and pollutants at trace levels down to 0.1 ppb or below in the water samples. An excellent precision for the common OCP pesticide residues was demonstrated using lindane as a representative compound.

The chosen analytical setup for the TRACE 1110 GC in split mode provides distinct analytical and economic advantages. The use of the split mode allows shorter analysis time for increased sample throughput and the best possible separation amongst closely eluting peaks.

References

[1] Pasha, A. Analysis of Pesticide Residues in Drinking Water. *Indian Food Industry Journal*, 2003, 22*(4)*, 36-39.

[2] Analysis of Pesticide Residues in bottled water, CSE Report No. CSE/PML/6/2002, Centre for Science and Environment (CSE), Pollution monitoring Centre, New Delhi.

[3] European Council Directive 80/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption.

[4] US EPA Method No. 508, Determination of Organohalide Pesticides in Water by Gas Chromatography with an ECD, Revision 3.1, Edited by J.W. Munch (1995).

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AN10350_E 09/13S

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